Energy Fuels XXXX, XXX, 000–000 · DOI:10.1021/ef900799c

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High-Density Renewable Fuels Based on the Selective Dimerization of Pinenes

Benjamin G. Harvey,* Michael E. Wright, and Roxanne L. Quintana

United States Navy—Naval Air Systems Command (NAVAIR), Naval Air Warfare Center, Weapons Division (NAWCWD), Research Department, Chemistry Division, China Lake, California 93555

Received July 27, 2009. Revised Manuscript Received October 1, 2009

High-density fuel candidates have been synthesized in up to 90% yield from β-pinene, a renewable strained bicyclic compound derived from wood and plant sources. The process is based on the heterogeneous acidic catalysts Montmorillonite-K10 and Nafion, which promote selective isomerization and dimerization of pinenes under moderate conditions (100 °C and atmospheric pressure). Montmorillonite-K10 was shown to be a highly active catalyst for dimerization but was also active in the ring opening of β-pinene followed by dehydrogenation to produce *p*-cymene, which limited the yield of the dimer to ca. 75%. Nafion was capable of producing dimers in up to 90% yield primarily through isomerization followed by dimerization. Amberlyst-15, a common industrial catalyst had very poor activity and conversion even at 150 °C. The dimer mixtures were upgraded through hydrogenation over PtO_2 and fractional distillation. The synthesized fuels have a density of 0.94 g/cm^3 and a net volumetric heating value of 39.5 MJ/L (141 745 BTU/gallon). These values are nearly identical to those for the widely used tactical fuel JP-10 (primarily composed of exotetrahydrodicyclopentadiene), suggesting that these renewable fuels may have applications for rocket propulsion.

Introduction

The efficient production of fuels and plastics from renewable sources is one of the key challenges of this century.[1] Over the last several years, impressive progress has been made in the development of renewable replacements for widely used transportation fuels, such as gasoline and diesel fuel. However, high-density, petroleum-based, tactical fuels, such as JP-10 and RJ-5 (Figure 1, exotetrahydrodicyclopentadiene and norbornadiene dimers, respectively), will be difficult to replace given their remarkable densities of 0.94 and 1.08 g/mL respectively, and, in the case of RJ-5, significant ring strain contributing to a high heat of combustion (Table 1). Bulk agricultural waste products, such as cellulose and lignin, are often targeted as feedstocks for the production of renewable fuels. However, even branched chain saturated hydrocarbon fuels, which can be derived from cellulosic butanol (Biojet), only have a density of 0.78 g/mL,[2a] while saturated linear fuels produced from syngas have a density of 0.75 g/mL.[2c] Although these alternative fuels compare favorably to high flashpoint jet fuels, such as JP-5, their low densities are reflected in their relatively poor volumetric heating values, with renewable Biojet capable of producing only 34.3 MJ/L[2a] compared to JP-10 at 39.6 MJ/L and RJ-5 at 44.9 MJ/L.[3]

In addition to having outstanding volumetric heating values, tactical fuels must have low freezing points for use at high altitudes and in cold climates. These restrictions have limited the use of RJ-5 as a standalone fuel, notwithstanding its impressive heating value. On the basis of these challenging requirements, it is clear that abundant, specialized, and renewable feedstocks will be necessary to produce tactical fuel replacements. A promising technological route for addressing this challenge is the use of plants and microbes to selectively produce specific organic molecules in a continuous process. In effect, this approach would result in the upgrading of low-value feedstocks, such as CO_2, glucose, and cellulose, to custom organic molecules and high-value fuels that lie along an established biosynthetic pathway. Potential targets for this bioengineering approach are α- and β-pinene (Figure 2). These molecules are versatile natural products that are produced by a wide variety of trees and other plant life. They have industrial applications as solvents, resin precursors,[4] pharmaceutical synthons,[5] and are used in the production of cosmetics and perfumes.[6] Because of their compact structures and reactive olefin functionalities, these molecules have significant potential as feedstocks for high-density renewable fuels.[2b,7] Both molecules have bicyclic structures incorporating cyclobutanes that possess on the order of 100 kJ/mol of

*To whom correspondence should be addressed. E-mail: benjamin.g.harvey@navy.mil.

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Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **2009**	2. REPORT TYPE	3. DATES COVERED **00-00-2009 to 00-00-2009**
4. TITLE AND SUBTITLE **High-Density Renewable Fuels Based on the Selective Dimerization of Pinenes**		5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **United States Navy - Naval Air Systems Command (NAVAIR),Naval Air Warfare Center, Weapons Division (NAWCWD), Research Department,Chemistry Division,China Lake,CA,93555**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**		
13. SUPPLEMENTARY NOTES		
14. ABSTRACT		
15. SUBJECT TERMS		

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**7**	

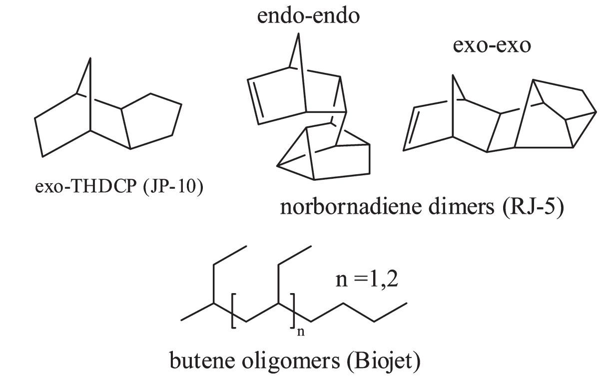

Figure 1. Structures of high-density fuels compared to a renewable jet fuel (Biojet).[2a]

Table 1. Selected Data for High-Density Fuels

property	Biojet	JP-10	RJ-5
heating value (MJ/L)	34.3	39.6	44.9
(BTU/gallon)	123 000	142 000	161 000
freezing point (K)	< 213	< 194	> 255
specific gravity (g/mL)	0.78	0.94	1.08

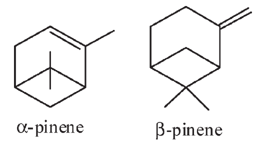

Figure 2. Structures of α- and *β*-pinene.

ring strain.[8] This results in a higher heat of combustion than unstrained or linear molecules with similar molecular weights. The volumetric heat of combustion can be further improved through dimerization, which significantly increases the density of the mixture. Industrially, the dimerization of olefins is often carried out with environmentally unfavorable catalysts, such as sulfuric or hydrofluoric acid. These catalysts are corrosive and dangerous to work with, and their use results in the production of large amounts of waste that must be either treated or recycled, resulting in increased energy demands. In contrast, the use of solid acid catalysts provides several advantages over conventional liquid acid systems. For example, these heterogeneous catalysts are typically much less corrosive, safer to work with, easier to separate, and more easily recycled than liquid acid systems.[9,27]

Dimerization of α- and *β*-pinene has been reported using Bronsted acid catalysts, such as phosphoric acid,[10] Lewis acid catalysts, such as BF_3,[11] and acidic zeolites.[12] Unfortunately, these previous studies have revealed complicated product distributions, moderate yields, and provided little evidence with regard to the structures of the dimers. In an effort to selectively produce dimer mixtures with potential uses as high-density renewable fuels using environmentally friendly catalysts, we have studied the reactions of *β*-pinene with the acidic heterogeneous catalysts Montmorillonite K10 (MMT-K10),

Table 2. Catalysts for the Dimerization of *β*-Pinene

catalyst	temperature (°C)	time	products	dimer yield
MMT-K10	0−30	4 h	isomers	trace
MMT-K10	100	1 h	dimer/isomers	76%
MMT-K10	150	1 h	dimer/trimer/ isomers	68%
Amberlyst-15	ambient	24 h	NR	−
Amberlyst-15	150	3 h	isomers	trace
Nafion	ambient	24 h	NR	−
Nafion	100	2 h	dimer/isomers	83%
Nafion	100	6 h	dimer/isomers	> 90%
Nafion	150	2 h	dimer/isomers/ trimer	77%
H_2SO_4 (98%)	0	10 min	polymer	−
H_2SO_4 (50%)	0	10 min	polymer	−

Amberlyst-15, and Nafion. The use of these catalysts allows for a study of the dimerization of *β*-pinene with sulfonic-acid-functionalized catalysts across a range of acidities and, in the case of MMT-K10, the effect of a catalyst with both Bronsted and Lewis acid sites.

Experimental Section

Nafion (Aldrich) was precipitated from a 5% water/alcohol dispersion by the addition of CH_2Cl_2 and ether, followed by filtration and drying under vacuum (4 Torr) at ambient temperature.[13] MMT-K10 (Aldrich) and dry Amberlyst-15 (Aldrich) were used directly from the bottle. (1*S*)-(−)-*β*-Pinene (Aldrich) was typically used without further purification, or after an extended storage time, it was distilled from CaH_2 under a nitrogen atmosphere. Product mixtures were analyzed with an Agilent 6890-GC/5973-MS to determine chemical compositions. The density of the product mixtures was measured with an Anton Parr DMA-35N density meter. Heat of combustion and elemental analyses were conducted by the Southwest Research Institute.

***β*-Pinene Dimerization.** Note that the dimerization reaction is very exothermic, particularly when MMT-K10 is used as the catalyst. Runaway reactions can occur with both MMT-K10 and Nafion, especially with concentrated solutions or in the absence of a suitable heat sink. Slow addition of *β*-pinene to a refluxing reaction mixture at 100 °C was determined to be the safest method of addition. In a typical procedure, the solid acid catalyst (100 mg of Nafion or 500 mg of MMT-K10) was slurried in 10 mL of *n*-heptane under a nitrogen atmosphere and heated to reflux. *β*-Pinene (35 g) was then added dropwise to the slurry, and the reflux was maintained with external heating for the remainder of the reaction; additional reactions were conducted from 0 °C up to the reflux temperature of *β*-pinene (Table 2). Dimer mixtures were hydrogenated with 1 wt % PtO_2 under 1−2 psig of hydrogen for a period ranging from 12 to 24 h. Subsequent distillations were carried out under reduced pressure (4 mmHg).

Results and Discussion

α- and *β*-pinene have net heats of combustion of 132 300 and 132 500 BTU/gallon, respectively.[14] This can be compared to JP-10 at 142 000 BTU/gallon (Table 3).[3] It should be

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(14) Calculated on the basis of the experimental heat of formation, as reported in http://webbook.nist.gov.See also Hawkins, J. E.; Eriksen, W. T. *J. Am. Chem. Soc.* **1954**, *76*, 2669.Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

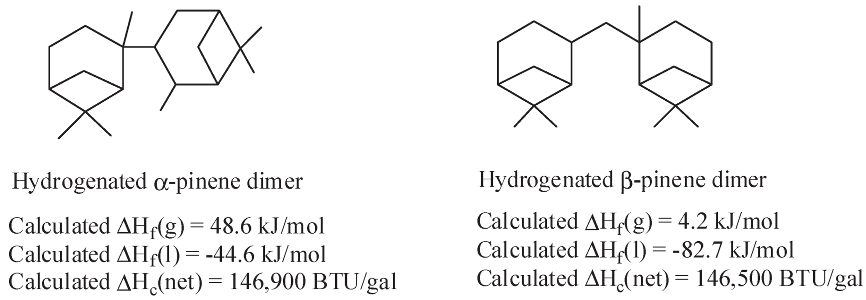


Figure 3. Structures of target dimer molecules and selected calculated properties.

Table 3. Selected Properties of JP-10 and α- and β-Pinene

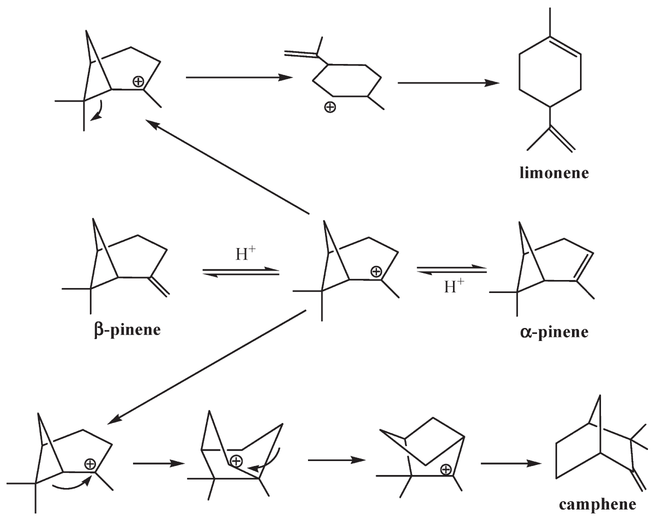
property	β-pinene	α-pinene	JP-10
density	0.859	0.858	0.94
ΔH_f(g) (kJ/mol)	35.8	30.2	−96.6[a]
ΔH_f(l) (kJ/mol)	−7.66	−16.4	−133.8[b]
ΔH_c (BTU/gallon)[c]	132 500[d]	132 300[d]	142 000

[a] Semi-empirical calculation (MOPAC AIM1). [b] Calculated from the experimental heat of combustion. [c] Net heat of combustion. [d] Calculated from the experimental heat of formation.

noted that both pinene molecules also have positive gas-phase heats of formation because of strain energy. A clear path to improve the volumetric heating value of these natural products is selective dimerization that would both increase the density and maintain the ring strain of these molecules. Two target dimer molecules are shown in Figure 3. Semi-empirical calculations for both of these molecules give positive gas-phase heats of formation and impressive values for the net heat of combustion (on the basis of a density of 0.94 g/cm^3): 146 900 and 146 500 BTU/gallon for the hypothetical hydrogenated α- and β-pinene dimers, respectively.[15] These calculations suggest that dimerized pinenes have the potential to have heating values exceeding that of JP-10. Given the favorable potential net heat of combustion for these pinene dimers, reactivity studies with the acidic catalysts MMT-K10, dry Amberlyst-15, and Nafion were explored.

Montmorillonite K10. We initially targeted MMT-K10 as a catalyst because of its low cost, abundance, and well-established reactivity.[16] MMT-K10 is a layered aluminosilicate functionalized with sulfonic acid groups through treatment with sulfuric acid. Its acidity can vary several orders of magnitude based on the amount of water present in the sample, and it has both Lewis and Bronsted acid sites.[17] The clay can delaminate or separate into particles as little as 1 nm in width and several hundred nanometers in length. Upon the addition of MMT-K10 to a flask containing β-pinene at room temperature, a vigorous reaction occurred. The catalyst immediately turned red and a rapid exotherm was observed. Without a heat sink, the reaction rapidly reached the boiling point of β-pinene. In an effort to more effectively control the reaction, the slow addition of β-pinene to a slurry of the catalyst in heptane at 0 °C under an inert atmosphere resulted in only a trace amount of isomers [detected by nuclear magnetic resonance spectroscopy (NMR)] and no significant dimer formation, suggesting that the isomerization reaction is very slow at that temperature. Removal of the ice bath led to an exotherm that was controlled by sequentially submerging the rapidly stirred flask in an ice bath, then removing the flask, and allowing the internal temperature to warm up to 30 (±5) °C. This was repeated several times until the temperature was stable at ambient temperature. At this point, the reaction was monitored by both NMR and gas chromatography/mass spectrometry (GC/MS), revealing that the principal reaction was isomerization to a mixture of camphene, limonene, and α-pinene, with some β-pinene remaining (Scheme 1). Small amounts of dimer, α- and γ-terpinene, and *p*-cymene were also observed, as well as a trace of oxidation products. The relative ratio of α-pinene/camphene/β-pinene/limonene was roughly 3:5:2:4. Heating the mixture to the reflux temperature of heptane led to a vigorous reaction with the production of significant amounts of hydrogen. After 1 h, the overall yield of dimer molecules was 76% by GC/MS, with the balance of the product represented by primarily *p*-cymene, camphene, and tricyclene. Extended heating times at the reflux temperature of heptane did not change the concentration of camphene in the reaction mixture, suggesting that MMT-K10 is a poor catalyst for camphene dimerization. Although camphene represents 35% of the initial isomerized product, it represents only ca. 10% of the final product mixture. This suggests that, although MMT-K10 is inefficient for the dimerization of camphene, it does promote the cross-coupling of

Scheme 1. Mechanism for the Isomerization of β-Pinene over MMT-K10



(15) Gas-phase data was calculated using MOPAC AIM1, while a liquid-phase net heat of combustion was calculated assuming a density of 0.94 g/mL and using double the value of the heat of vaporization of β-pinene given in Hawkins, J. E.; Armstrong, G. T. *J. Am. Chem. Soc.* **1954**, *76*, 3756.
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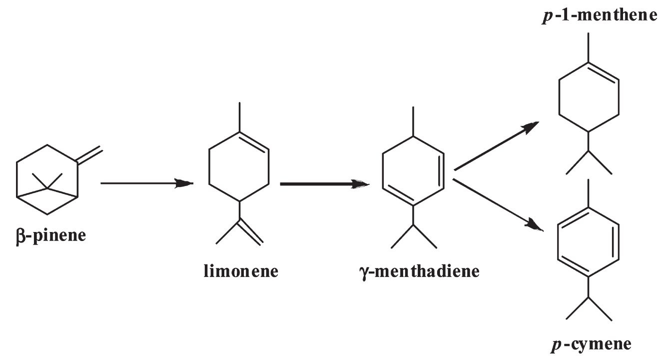
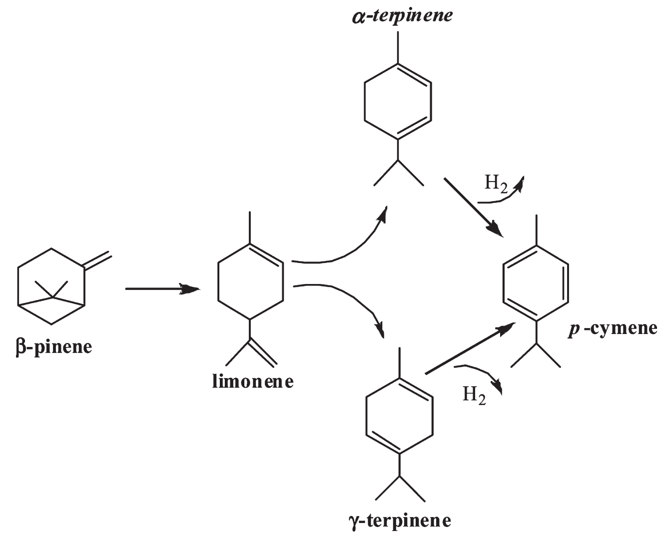
Scheme 2. Potential Mechanism for the Conversion of β-Pinene to *p*-Cymene



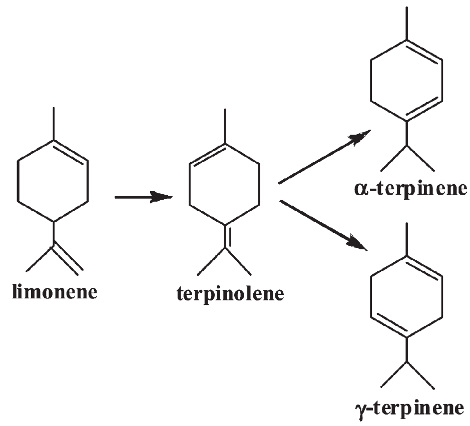
Scheme 3. Potential Mechanism for the Conversion of β-Pinene to *p*-Cymene



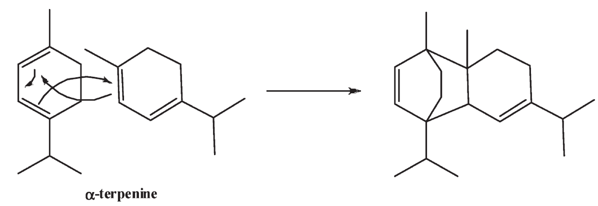
camphene with other isomers in solution. Another important product is *p*-cymene, which is derived from limonene. Previous studies suggest that the mechanism for formation of *p*-cymene proceeds through a rearrangement/disproportionation reaction in which limonene rearranges to terpinenes, which then disproportionate to *p*-cymene and a menthene, such as *p*-1-menthene (Scheme 2).[18] However, in our laboratory, copious production of hydrogen was evident at the reflux temperature of heptane. This supports a direct dehydrogenative mechanism (Scheme 3) that could be catalyzed by the clay or possibly by polyaromatic coke deposits on the catalyst surface.[19] To shed some light on the mechanism, (*R*)-(+)-limonene was added dropwise to a stirred slurry of MMT-K10 in refluxing heptane. After 1 h, an NMR spectrum was collected and it was observed that limonene, *p*-cymene, α- and γ-terpinene, and terpinolene were the primary low-molecular-weight components present. This result supports the second mechanism (Scheme 3), given that no evidence was observed for any menthene products. It is also of interest that the intermediate terpinolene was observed in the reaction mixture, suggesting that the isomerization reaction progresses in a step-like fashion (Scheme 4). Although no menthene products were observed in the NMR spectrum, GC/MS analysis of an MMT limonene mixture in heptanes that had been refluxed overnight revealed the presence of *p*-cymene and residual menthenes, primarily *p*-menth-3-ene and *p*-menth-1-ene. The presence of these particular menthenes was expected on the basis of the carbocationic mechanism of isomerization and the stability of intermediates with tertiary cationic centers. The data suggest that a competition exists between the first and second mechanism, with some disproportionation occurring through a dehydrogenative/hydrogenative mechanism and some direct loss of hydrogen ostensibly because of the slower rate of hydrogenation under these conditions. Additionally, many other potential reactants in solution, including dimer molecules, could react with the released hydrogen. The GC/MS analysis reveals that the dimer region is a complex mixture of peaks mainly with molecular weights of 272, while some peaks have m/z 274. It is unclear whether the molecule(s) represented by the m/z 274 peaks are produced by hydrogenation after dimerization of two monomers or if they are produced from the coupling of a monoolefin and a diolefin. A recent report has suggested that under somewhat harsher conditions (150 °C, acidic clay catalyst), terpinenes and other olefins undergo Diels–Alder reactions[18] (Scheme 5) promoted by the Lewis acidity of the catalyst.

Although the conversion to *p*-cymene is of interest, it limits the conversion of β-pinene to dimer products. In an attempt to efficiently control the heat of reaction and to selectively produce dimers incorporating ring-strained cyclobutane rings, β-pinene was added dropwise to a stirred slurry of MMT-K10 in refluxing heptane under a nitrogen atmosphere. Upon addition of the first drop, the slurry turned green and then rapidly converted to a red/brown suspension. After the addition, the mixture was refluxed for

Scheme 4. Stepwise Conversion of Limonene to Terpinenes through Terpinolene



Scheme 5. Example of a Potential Diels–Alder Dimerization Reaction of α-Terpinene[a]



[a] A similar reaction could occur between terpenines and a variety of olefins in solution.

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an additional hour. Interestingly, the NMR spectra and GC/MS chromatograms were indistinguishable from those obtained when β-pinene was added slowly at room temperature and then heated to refluxing heptane temperatures. This result suggests that the rate of isomerization at the elevated temperature is faster than the rate of dimerization of β-pinene. To determine the effect of even higher temperatures, β-pinene was added neat to the clay catalyst in an open flask maintaining a slow flow of nitrogen. The mixture was vigorously stirred and rapidly rose in temperature until vigorous gas evolution was evident. After the bubbling had mostly subsided, the flask was placed in an oil bath at 150 °C and further evolved gas was allowed to slowly escape through a bubbler. The distribution of products was similar to that observed at 100 °C with the addition of ca. 10% trimer, leading to a 70:10:20 ratio for dimer/trimer/low-molecular-weight products. This result suggests that the intermediate temperature is ideal, leading to a high conversion to dimer while limiting the formation of trimer or other heavier oligomers. The clay catalyst can be removed from the reaction mixture by filtration with some difficulty; however, because the catalyst is remarkably well-dispersed, it was often more convenient to separate the clay by centrifugation, followed by decantation.

Amberlyst-15. Although MMT-K10 was found to be an efficient dimerization catalyst, in an attempt to produce a dimer mixture with less isomerized products and more molecules maintaining strained ring systems, Amberlyst-15, a sulfonic-acid-functionalized cross-linked polystyrene resin, was investigated to determine its catalytic activity for the dimerization of β-pinene. Unlike MMT-K10, upon the addition of neat β-pinene to beads of Amberlyst-15 under nitrogen, no reaction at room temperature occurred even upon reaction times of 48 h. This difference in activity may be due to the presence of Lewis acidic sites present in MMT-K10, which may allow for coordination and isomerization of β-pinene at low temperatures.[18] Upon heating to 150 °C for 3 h, a mixture of primarily β-pinene and camphene were present with traces of p-cymene and dimer. Given the slow reaction rate, negligible conversion to dimer, and high reaction temperature, Amberlyst-15 was not studied in further detail.

Nafion. Nafion is a perfluorinated sulfonic acid resin that is often denoted as being a superacid, a compound with acidity greater than concentrated sulfuric acid. Unlike MMT-K10, which maintains a high surface area and can delaminate at elevated temperatures to yield easily dispersible nanosized catalyst particles, Nafion does not disperse well in nonpolar solvents.[20] This limits the surface area of the catalyst and the relative amount of active sites in contact with the reaction medium. Nafion can be well-dispersed on inorganic supports, and such composites have been shown to be effective for a variety of acid-catalyzed processes.[21−26] However, the presence of the support can often influence the reactivity through interaction of surface hydroxyl groups on the support with the sulfonic acid groups of the polymer.[27] The catalyst was prepared by precipitation of a Nafion dispersion from water/alcohol and was dried under vacuum (4 mmHg) at ambient temperature to yield a flocculent white powder. In a manner similar to Amberlyst-15, Nafion showed virtually no reactivity at room temperature for reaction times as long as 24 h. When neat solutions of β-pinene were heated with Nafion to 90 °C with stirring, no reaction occurred for an extended period of time, typically 20−50 min, and then quite suddenly, the Nafion turned a dark red color and a rapid exothermic reaction ensued with evolution of gas. Upon an additional hour at 90 °C, ^{1}H NMR spectroscopy revealed that the only remaining low-molecular-weight molecules were camphene and a small amount of p-cymene. Interestingly, when MMT-K10 was used as a catalyst, nearly 10 times more p-cymene was produced. This result suggested that either the ring-opening mechanism that converts β-pinene to limonene does not readily occur with Nafion at these reaction temperatures or that the rate of dimerization of limonene over Nafion is substantially faster than the dehydrogenation reaction to produce p-cymene. To differentiate between the two possibilities, a reaction was stopped prior to completion and an NMR spectrum was collected. Camphene was the dominant monomeric olefin, with small, nearly equal amounts of β-pinene and limonene. At this point in the reaction, p-cymene was not observed in the ^{1}H NMR spectrum. It appears from the data that the primary mechanism over Nafion is conversion to camphene and other isomers concomitant with homo- and cross-dimerization of the olefin mixture. Upon further reaction, only residual camphene is present, which dimerizes somewhat sluggishly over Nafion; however, unlike MMT-K10, continued reaction at 100 °C led to the conversion of camphene to dimer molecules. To determine the effect of higher temperatures, the reaction was run neat at 150 °C using Nafion as the catalyst. Interestingly, p-cymene was formed in amounts similar to that observed for MMT-K10, in addition to the observance of ca. 10 wt % trimer. This suggests that for Nafion the dehydrogenation of limonene to p-cymene is favored at higher temperatures, while dimerization is favored at lower/intermediate temperatures. As with MMT-K10, it appears that a temperature of 100 °C is ideal for maximizing the amount of dimer produced. For all of the Nafion reactions, the catalyst could be removed by simple decantation and reused at least 3 times without significant loss of activity. Given sufficient reaction time, yields of dimer as high as 90% were obtained. The GC/MS chromatogram of the product mixture revealed a broad distribution of dimer molecules (Figure 4) with the majority having m/z 272. Small amounts of other molecular weights, such as 274 and 288 were also observed, with the former being attributed to the coupling of terpinenes and menthenes and the latter attributed to isobornyl ether, which has been shown to be an oxidation product produced from camphene with heteropolyacidic catalysts[28] (Scheme 6). As mentioned previously, at the conclusion of the reaction, the Nafion takes on a deep red hue. Several CH_2Cl_2 washes did not remove the color; however, with the exception of some very weak C−H

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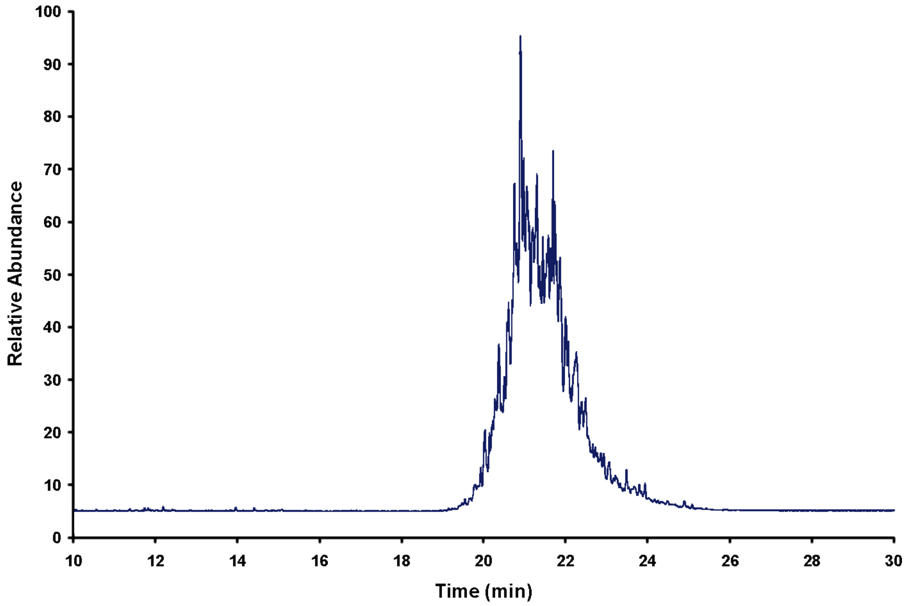

Figure 4. Gas chromatogram of hydrogenated β-pinene dimers catalyzed by Nafion.

stretches, the IR spectra of used Nafion and pristine Nafion were essentially identical.

Upgrading of Dimer Mixtures. The dimer yield varied depending upon the catalyst and conditions. Yields of dimer were reduced when MMT-K10 was used because of an increase in the amount of *p*-cymene produced and the inability of MMT-K10 to efficiently homodimerize camphene. The amount of dimer was also heavily influenced by the reaction temperature, in that higher temperatures produced trimer molecules and potentially other higher oligomers. Reactions run at >140 °C produced colored solutions ranging from dark yellow to orange−red depending upon the reaction time, suggesting that polymeric or conjugated mixtures were being produced. Reactions controlled at ca. 100 °C with refluxing heptanes gave colorless mixtures when MMT-K10 was used as the catalyst and pale yellow mixtures when Nafion was used.

For potential use as fuels, these dimer mixtures must be hydrogenated to increase their stability. The reaction mixtures were simply decanted and transferred to another flask for hydrogenation; no workup or caustic treatment was required. PtO_2 was used as the hydrogenation catalyst under mild H_2 pressures because it has been shown to be a very efficient catalyst for hindered olefins.[2a,b] The resulting dimer mixtures were then placed under reduced pressure to remove *n*-heptane and low-molecular-weight products, such as camphane (MMT-K10 catalyst), and then vacuum distilled to produce a dimer cut. Fractional vacuum distillation gave a trace of a low boiling fraction, consisting of primarily camphane and *p*-cymene, followed by a colorless dimer fraction (bp 116−122 °C, 4 mmHg) and leaving a small amount of resinous solid residue comprising a mixture of dimer and traces of other heavier oligomers. Isolated, distilled yields of the dimer fraction were greater than 80% on a 30 g scale (when Nafion was used), while for larger operations, a yield of up to 90% based on the GC/MS data seems reasonable because of more efficient distillations. Although higher oligomers limit the yield of dimer molecules, they have industrial uses as resins and adhesives.[29]

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Scheme 6. Acid-Catalyzed Conversion of Camphene to Diisobornyl Ether

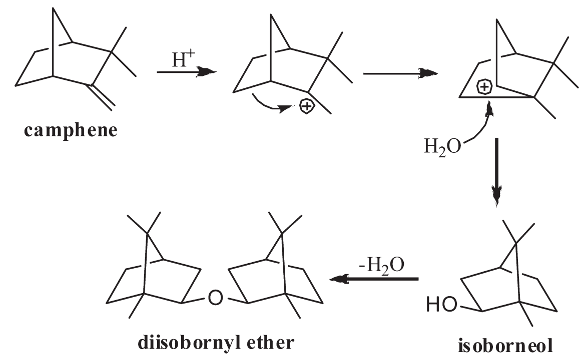

Table 4. Measured Values of Hydrogenated Pinene Dimers

property	value
density (g/cm^3)	0.938
heating value (MJ/L)	39.5
(BTU/gallon)	141 745
pour point (°C)	−30
sulfur (ppm)	0.5
carbon (%)	87.72 (calculated for $C_{20}H_{34}$: 87.52)
hydrogen (%)	12.12 (calculated for $C_{20}H_{34}$: 12.48)

The measured properties of the fuel are listed in Table 4. The density of the hydrogenated dimer mixture prepared with Nafion was 0.938 g/cm^3, similar to JP-10 at 0.94 g/cm^3. The net heat of combustion of the dimer mixture was 141 745 BTU/gallon, virtually identical to JP-10 (142 000 BTU/gallon), while the pour point was measured to be −30 °C, substantially higher than JP-10, which has a freezing point of −79 °C. A recent paper focused on the synthesis of pinene dimers with BF_3 as the catalyst reported that the low-temperature (−15 °C) viscosities of a variety of hydrogenated, mixed terpene dimers are in the range of 18−30 × 10^3 cP.[11] These high viscosities are mainly due to the close proximity of the freezing points (estimated as -23 ± 3 °C) to the sampling temperature. These values can be compared to JP-10 with a reported viscosity of 7.3 cP at −15 °C.[30] Clearly, fuels made solely from pinene dimers by an acid-catalyzed process are not yet suitable for high-altitude applications given current engine configurations. Of course specialty fuels based on norbornadiene dimers, which have high melting points, have been considered as rocket fuel components in combination with a low freezing component.[31] In a similar manner, one could envision pinene dimer/JP-10 blends as a partially renewable fuel or pinene dimer/monomer mixtures as a fully renewable replacement for petroleum-based, high-density fuels.

Conclusions

An effective method for producing high-density fuel candidates from pinenes has been developed. MMT-K10 is an efficient catalyst for the reaction, although significant amounts of *p*-cymene and camphene produced as byproducts limit the overall yield to slightly less than 80%. Surprisingly, the commonly used ion-exchange resin, Amberlyst, only slowly isomerized β-pinene and produced virtually no dimer. In contrast, Nafion was an excellent catalyst for pinene dimerization and was capable of producing dimers in up to 90% yield. Pinene dimers synthesized with these heterogeneous catalysts have a density and net heat of combustion comparable to JP-10.

Acknowledgment. The authors thank Andrew Chafin for gas-phase heat of formation calculations and NAWCWD and the Office of Naval Research (In-House Laboratory Independent Research Program) for funding this work.

Note Added after ASAP Publication. Due to a production error, this paper published ASAP November 13, 2009 without listing reference 2; the corrected version published ASAP November 18, 2009.

Supporting Information Available: Experimental details for the synthesis of hydrogenated pinene dimers and ^{1}H NMR spectra of intermediate and final reaction mixtures before and after hydrogenation. This material is available free of charge via the Internet at http://pubs.acs.org.

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